Quantum Monte Carlo method for real materials using auxiliary fields

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OUTLINE

- Introduction to Quantum Monte Carlo methods
- Auxiliary field QMC: Slater determinant random walks
  - Motivation
  - Formulation as a ground-state method
- Phase/sign problem
- Approximate solution
- Applications to molecules & solids
  - results for sp & d-electron systems
  - good agreement with experiment
- Summary and Outlook

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Reference

Zhang and Krakauer, *Phys. Rev. Lett.* ***90****, 136401 (2003)*

Why Quantum Monte Carlo?

- Offers the possibility of accurate and robust calculations spanning many material types
- Density-functional methods (LDA, GGA, …) are very successful except for strongly correlated materials.
- Even for weak to moderate correlated materials, some desired properties may be sensitive to small errors resulting in crucial and qualitative differences in predicted properties (e.g. the “volume” problem in ferroelectrics).
- QMC methods *scale algebraically* with number of electrons.

Basic idea of QMC

Start with an initial state given by a trial wave function:

$$\left|\Phi^{(0)}\right\rangle = \left|\Psi_T\right\rangle.$$

Iteratively project out the *N*-particle ground-state $\left|\Psi_G\right\rangle$:

$$\left|\Phi^{(n+1)}\right\rangle = e^{-\tau H}\left|\Phi^{(n)}\right\rangle$$

$$\left|\Phi^{(n)}\right\rangle \to \left|\Psi_G\right\rangle \quad (n \to \infty)$$

$$H = H_{1-\text{part}} + H_{2-\text{part}}$$

$$e^{-\tau H} = e^{-\tau H_1/2} e^{-\tau H_2} e^{-\tau H_1/2} + O(\tau^3)$$

Imaginary-time (n x τ) projection is realized stochastically by *random walks* in an appropriate Hilbert space.

QMC Random Walks

I) Diffusion Monte Carlo (DMC): random walks in coordinate space (*standard for real materials*)

The *N*-particle many-body wave function is sampled by *walkers* in coordinate space: $\left|\mathbf{R}\right\rangle = \left|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right\rangle$,

$$\left|\Psi_G\right\rangle = \sum_{\mathbf{R}} w_{\mathbf{R}} \left|\mathbf{R}\right\rangle.$$

II) Auxiliary-Field QMC (AFQMC): random walks in Slater-determinant space (*mostly lattice models*)

Walkers are *N*-particle Slater determinants: $\left|\phi\right\rangle$,

$$\left|\Psi_G\right\rangle = \sum_{\phi} w_{\phi} \left|\phi\right\rangle.$$

Why auxiliary-field quantum Monte Carlo (AFQMC)?

- A QMC approach using an arbitrary one-particle basis: shares same machinery as in mean-field (HF or DFT) calculations
  - The one-particle problem is solved exactly with no statistical error
  - Correlation effects are obtained by building stochastic ensembles of independent-particle solutions
  - Non-local pseudopotentials: straightforward to implement
  - Planewaves (implemented) and PAWs (not yet) lead to favorable algorithmic scaling as in DFT methods
- Opportunities for better approximations to treat sign problem, *e.g.* for weak to intermediate correlation?
- Each walker is a full mean-field wave function. Could this allow for more convenient calculations of expectation values (density, force, correlation functions)?

AFQMC Methodology

Ground state projection from trial wave function:

$$e^{-\tau H_1/2}\, e^{-\tau H_2}\, e^{-\tau H_1/2} \left|\Phi^{(n)}\right\rangle = \left[\int e^{-\frac{\sigma^2}{2}} B(\sigma) d\sigma\right] \left|\Phi^{(n)}\right\rangle$$

H-S transform

$$B(\sigma) \equiv e^{-\tau H_1/2}\, e^{-\sqrt{\tau}\sigma.\mathbf{v}}\, e^{-\tau H_1/2}$$

v is a 1-body *complex* operator in general

Becomes a random walk in Slater-determinant space: $\left|\phi^{(n+1)}\right\rangle \leftarrow B(\sigma)\left|\phi^{(n)}\right\rangle.$

Produces a Monte Carlo sample of the ground state: $\left|\Psi_G\right\rangle = \sum_\phi w_\phi \left|\phi\right\rangle.$

Phase/sign problem: fluctuating phases of determinants cause numerical accuracy to decay exponentially.

A simple *constraint* does not work well: $\mathrm{Re}\left(\left\langle \Psi_T \middle| \phi \right\rangle\right) > 0.$

New AFQMC Method: Importance Sampling Transformation

Propagator is modified:

$$\left|\phi'(\sigma)\right\rangle \leftarrow \left\langle \Psi_T \middle| \phi'(\sigma)\right\rangle B(\sigma-\bar{\sigma})\frac{\left|\phi\right\rangle}{\left\langle \Psi_T \middle| \phi\right\rangle}.$$

A shift or "*force bias*" $\bar{\sigma}$ (Rom '97) is introduced, and the propagator can be written in terms of the *local energy* E_L:

$$\left|\phi'(\sigma)\right\rangle \leftarrow e^{-\tau E_L(\phi)} e^{-\tau H_1/2} e^{-\sqrt{\tau}(\sigma-\bar{\sigma}).\mathrm{v}} e^{-\tau H_1/2}\left|\phi\right\rangle;$$

$$E_L(\phi) \equiv -\frac{\left\langle \Psi_T \middle| H \middle| \phi\right\rangle}{\left\langle \Psi_T \middle| \phi\right\rangle}; \qquad \bar{\sigma} \equiv -\frac{\left\langle \Psi_T \middle| \sqrt{\tau}\mathrm{v} \middle| \phi\right\rangle}{\left\langle \Psi_T \middle| \phi\right\rangle}.$$

Weights evolve as:

$$w_{\phi'} \leftarrow e^{-\tau E_L(\phi)} w_\phi.$$

- $\bar{\sigma}$ and E_L are complex
- neglect $\mathrm{Im}(E_L)$ since E_L is real as $\left|\Psi_T\right\rangle \rightarrow \left|\Psi_G\right\rangle$

Phaseless walkers, continued

Produces a Monte Carlo sample of *phaseless determinants* with *real* weights:

$$\left|\Psi_G\right\rangle \doteq \sum_\phi w_\phi \frac{\left|\phi\right\rangle}{\left\langle \Psi_T \middle| \phi \right\rangle}.$$

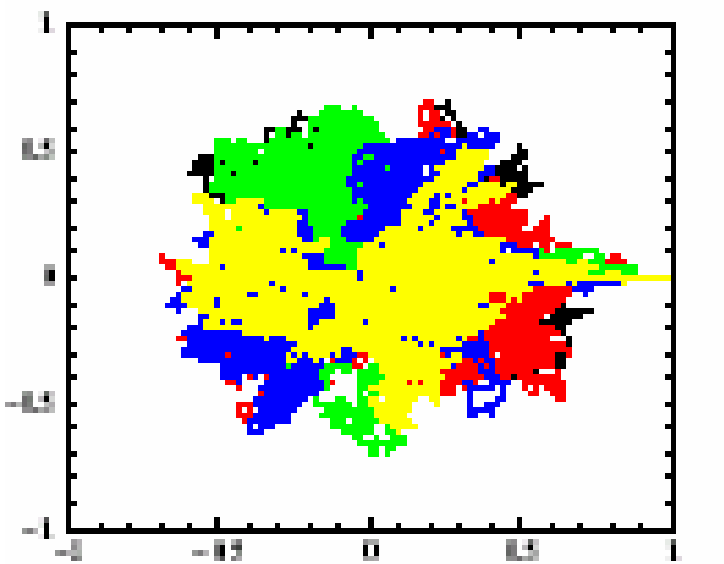
The *mixed* estimator for the ground state energy is phaseless:

$$E_G = \frac{\left\langle \Psi_T \middle| H \middle| \Psi_G \right\rangle}{\left\langle \Psi_T \middle| \Psi_G \right\rangle} \doteq \frac{\sum_\phi w_\phi E_L(\phi)}{\sum_\phi w_\phi}.$$

One more problem:

Walker distribution

in the $\langle \Psi_T | \phi \rangle$-complex plane



$\mathrm{Im}\langle \Psi_T | \phi \rangle$

$\mathrm{Re}\langle \Psi_T | \phi \rangle$

In random walk $|\phi\rangle \rightarrow |\phi'\rangle$,

$\langle \Psi_T | \phi \rangle = |\langle \Psi_T | \phi \rangle| \exp(i\theta)$

$\langle \Psi_T | \phi' \rangle = |\langle \Psi_T | \phi' \rangle| \exp(i\theta')$,

a *finite* density of walkers develops at the *origin*, where the importance function

$\dfrac{\langle \Psi_T | \phi' \rangle}{\langle \Psi_T | \phi \rangle}$ *diverges*.

A *solution*: "project" diffusion onto 1D by reducing the walker's weight by $\cos(\theta' - \theta)$.

Features of New AFQMC Method

- The mixed estimator for the ground state energy is not variational, *i.e.* no upper bound property on

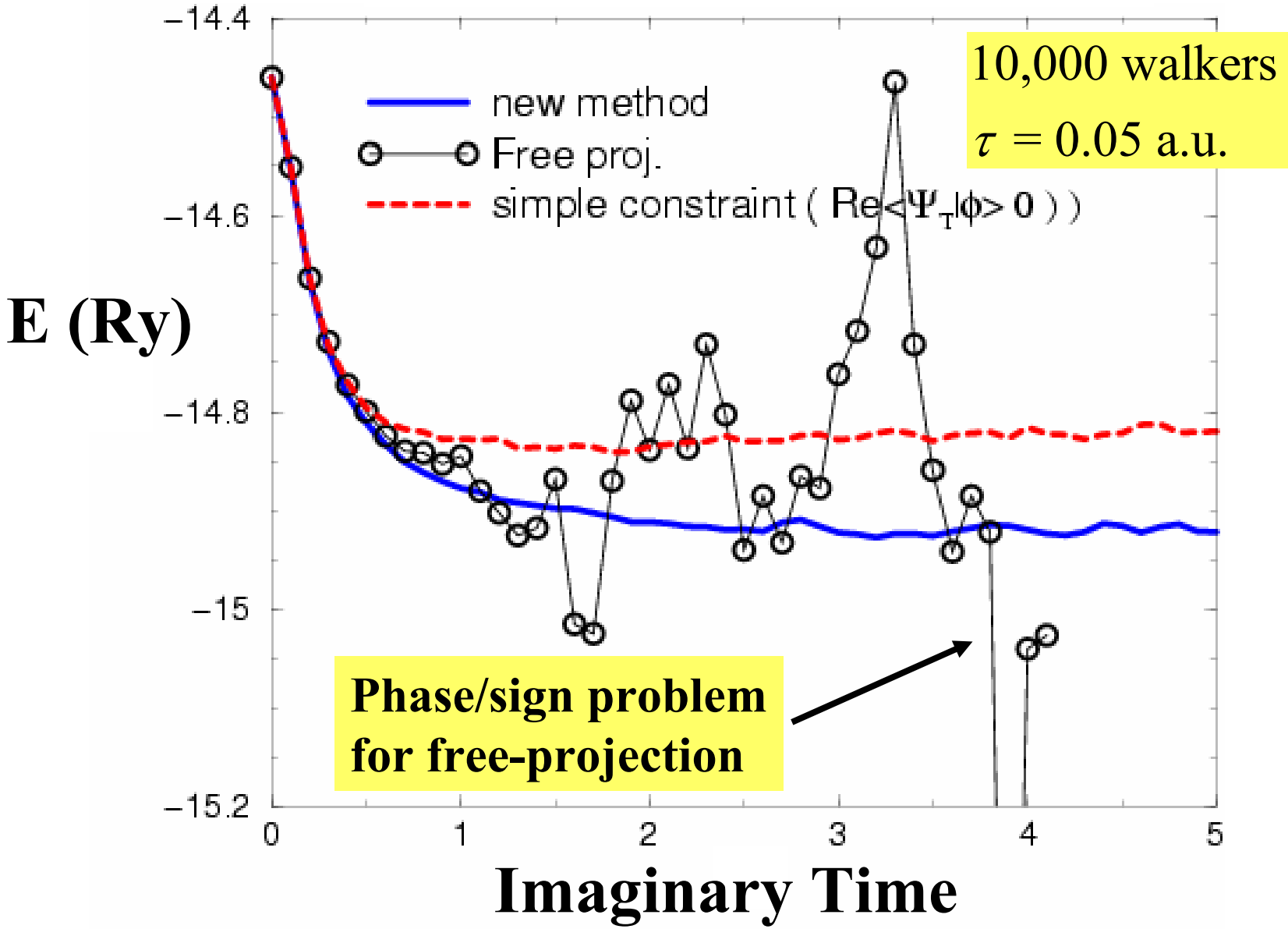
$$E_{MC} = \frac{\sum_{\phi} w_{\phi} E_L(\phi)}{\sum_{\phi} w_{\phi}}.$$

- Reduces to the *constrained-path* random walk [Zhang *et al*., PRB 55, 7464 (97)] for *real* Hubbard-Stratonovich fields:

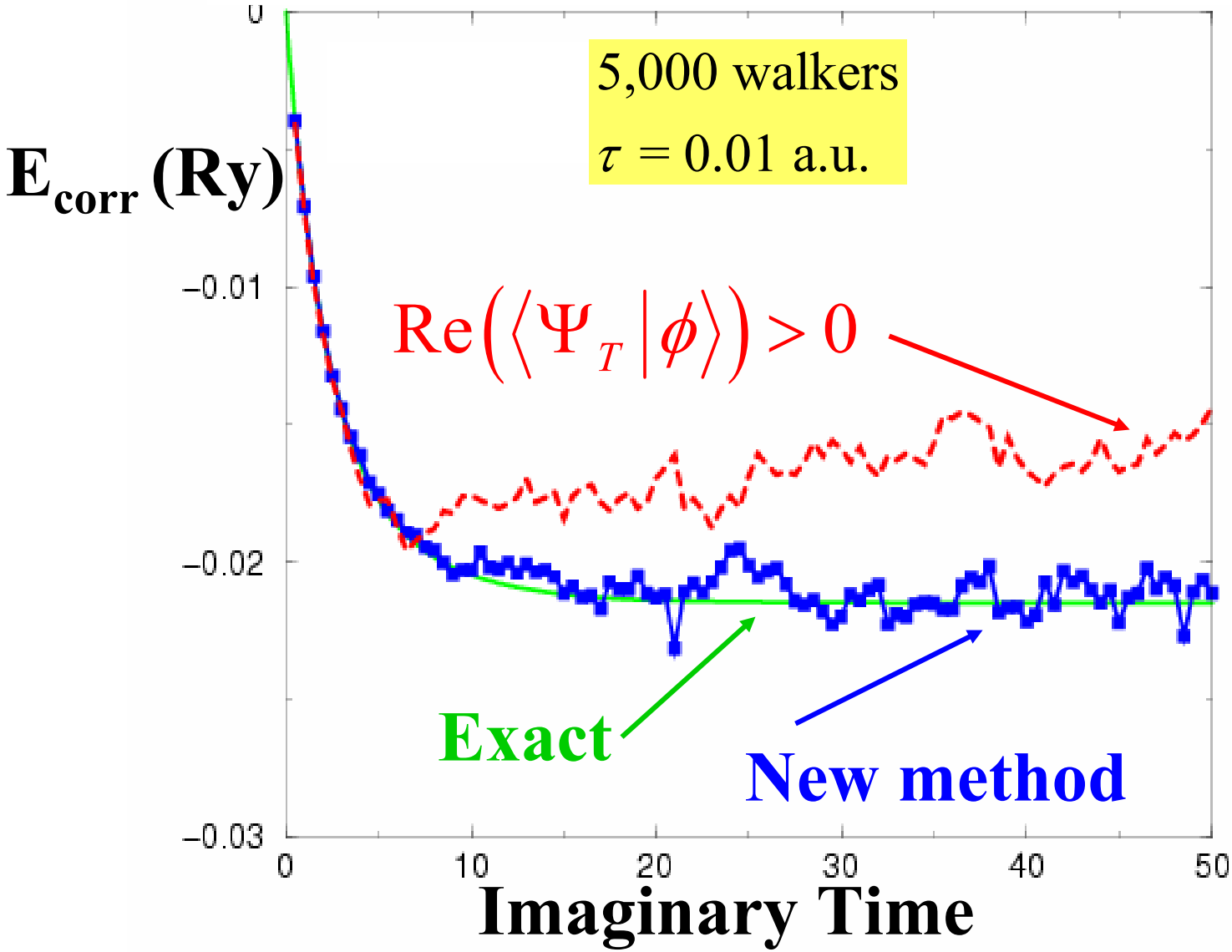
$$\langle \Psi_T | \phi \rangle > 0.$$

- Leads to *fixed node* DMC formalism when expressed as random walk in real-space *(*Hubbard-Stratonovich decomposition of *kinetic energy*).

fcc Si: 2-atoms, 8 electrons



Jellium: 2 electrons, $r_s = 10$



Some methodological details

$$H = K + V_{\text{e-ion}} + V_{\text{e-e}} + V_{\text{ion-ion}}$$

$$K = \sum_{\mathbf{G}} \mathbf{G}^2 c_{\mathbf{G}}^{\dagger} c_{\mathbf{G}}$$

$$V_{\text{e-ion}} = V_{\text{e-ion}}^{L} + V_{\text{e-ion}}^{NL}$$

$$V_{\text{e-ion}} = \sum_{\mathbf{Q}} V_{\text{L}}(\mathbf{Q}) \rho(\mathbf{Q}) + \sum_{\mathbf{G},\mathbf{G}'} V_{\text{NL}}(\mathbf{G},\mathbf{G}') c_{\mathbf{G}}^{\dagger} c_{\mathbf{G}'}$$

$$V_{\text{e-e}} = \frac{1}{\Omega} \sum_{\mathbf{Q}} \frac{4\pi}{Q^2} \rho^{\dagger}(\mathbf{Q}) \rho(\mathbf{Q}) \quad \text{and} \quad \rho(\mathbf{Q}) \equiv \sum_{\mathbf{G}} c_{\mathbf{G}+\mathbf{Q}}^{\dagger} c_{\mathbf{G}}$$

The Hamiltonian acts in the subspace spanned by planewaves with $G^2 \leq E_{cut}$.

Applying the HS propagator: an illustrative example

$$|\phi'\rangle \leftarrow \exp\left(\sqrt{\tau}\,\boldsymbol{\sigma}\bullet\mathbf{v}\right)|\phi\rangle = \exp\left(\sum_{\mathbf{Q}}\sqrt{\frac{4\pi}{Q^2}}\tau\,\sigma(\mathbf{Q})\rho(\mathbf{Q})\right)|\phi\rangle$$

$$|\phi'\rangle \leftarrow \sum_{n=0}^{n_{\max}}\frac{1}{n!}\left(\sqrt{\frac{4\pi}{Q^2}}\tau\,\sigma(\mathbf{Q})\rho(\mathbf{Q})\right)^n|\phi\rangle$$

Comments:

- done using iterated application of FFT's
- typically $n_{\max} \sim 4$ for realistic τ
- scales like $NM\ln(M)$
- in practice the local part of the pseudopotential, $V^L_{\text{e-ion}} = \sum_{\mathbf{Q}} V_{\text{L}}(\mathbf{Q})\rho(\mathbf{Q})$, is included with the above
- KB type $V^{NL}_{\text{e-ion}}$ is *separable* $\left[\exp(-\tau V^{NL}_{\text{e-ion}})\right]_{\mathbf{G},\mathbf{G}'} = \sum_{lm}\eta_l f^*_{lm}(\mathbf{G}')f_{lm}(\mathbf{G})$

Other details

- All results used a *single-determinant* trial wave function, with orbitals generated by ABINIT, with no further optimization
- OPIUM Kleinman-Bylander type LDA pseudopotentials
- Periodic boundary conditions
- All calculations done at *experimental* bond lengths or lattice parameter
- semi-core states included where appropriate,

  e.g. Ti(3s, 3p)

Si fcc cohesive energy (eV)

	16 atoms	54 atoms	∞
LDA	3.836	4.836	5.086
AFQMC	3.79(4)	4.51(3)	4.59(3)
DMC	(Kent *et al*. 1999)		4.63(2)
Exper.			4.62(8)

- 216 electrons; 5209 plane waves
- AFQMC Coulomb finite-size and zero-point corrections from Kent *et al*.

Summary: dimer binding energies (eV)

Dimer	LDA	AFQMC	DMC [1,2]	Exp
Be	0.53	0.07(2)	0.05(3)	0.11(1)
Si	3.88	3.12(8)	3.19(1)	3.21(13)
P	5.97	5.09(10)	4.68(1)	5.03
S	5.61	4.4(2)	4.34(1)	4.41

[1] Grossman, J. Chem. Phys. 2002, excluding Be.

[2] DMC Be: Schautz *et al*. 1998. Standard DMC does not bind with optimized Jastrow times a single Slater determinant.

Be_2 dissociation energy

Method	Energy (eV)	(at expt bond length 4.63 a.u.)
Hartree-Fock	unbound	
LDA [1]	0.53	
This AFQMC [1]	**0.07 (2)**	
Experiment	**0.11 (1)**	
DMC [2]	0.05(3)	Jastrow * multi-determinant trial w.f.
AF QMC [3]	0.0 (2)	phase problem

[1] 15x15x20 a.u.^{3} simulation cell; E_{cut} = 25 Ry; 9,467 PW's

[2] Schautz *et al. 19*98. Standard DMC does not bind with optimized Jastrow x single Slater determinant.

[3] Baer *et al., 20*00.

P_2 dissociation energy

Method	Energy (eV)	(at expt bond length 3.58 a.u.)
LDA [1]	5.97	
AFQMC [1]	**5.09(10)**	
Experiment	**5.03(2)**	
DMC [2]	**4.68(1)**	Jastrow * single-determinant trial w.f.
DMC [3]	**4.83**	Jastrow * 269 deter. for P2; 66 for P

[1] 14x14x18 a.u.^{3} simulation cell; E_{cut}=36Ry; 12,875 PW's

[2] Fixed-node DMC (Grossman, 2002).

[3] DMC Jastrow*multi-determinant trail w.f.'s, 66 determinants for P and 269 for P_2 (Grossman, 2002).

O_2 and PbO dissociation energy (eV)

Preliminary!

	LDA	AFQMC	DMC [1]	Exp
$E_B(O_2)$	7.6715	5.85 (35)	4.94 (02)	5.2
$E_B(PbO)$	6.1844	4.22 (67)	---	4.1

[1] Grossman, J. Chem. Phys. 2002.

- 20 electrons: O($2s^2$,$2p^4$); Pb($5d^{10}$,$6s^2$,$6p^2$)
- 10x11x17 a.u.^{3} simulation cell; E_{cut} = 50 Ry, 11171 planewaves
- experimental bond length

TiO binding energy (eV) - Preliminary!

DFT GGA-PBE	7.2	
DFT GGA-PW91 [1]	7.45	
DFT B3LYP [1]	6.62	
VMC (HF) [1]	**6.0(1)**	Jastrow * single-determinant trial w.f.
DMC (HF) [1]	**6.3(1)**	Jastrow * single-determinant trial w.f.
DMC (B3LYP) [1]	**6.9(1)**	Jastrow * single-determinant trial w.f.
DMC (MCSCF) [1]	**6.7(2)**	Jastrow * multi-determinant trial w.f.
AFQMC	**6.65(26)**	
Experiment [1]	**6.98**	

[1] Wagner & Mitas, *Chem. Phys. Lett*. **370**, 412 (2003).

- 18 electrons: O($2s^2$,$2p^4$); Ti($3s^2$, $3p^6$, $3d^2$, $4s^2$)
- 10 x 11 x 17 a.u.^{3} simulation cell; E_{cut} = 50 Ry, 11,197 planewaves
- bond length: PBE = 1.59 A; experiment = 1.62 A
- On a 667MHz Compaq Alpha processor, one time-step takes ~ 20 seconds per walker. About five days were required to achieve an accuracy of 0.2 eV using 200 walkers on 10 processors, about 80 Mb/processor.

Summary and Outlook

- Described a QMC method with auxiliary fields (AF) to treat *extended-interactions* (complex AF) without sign/phase problem (approximate).
- Simple trial wave function
- *Ab-initio* ground-state calculations using this framework show promising results.
- Potentially a method to systematically go beyond LDA while using much of its existing machinery

Summary and Outlook

To do:

- More applications: strongly correlated systems, ...
- Algorithm
  - Better pseudopotentials
  - Implementing calculation of expectation values
  - Further improvement: *e.g.* other 1-particle basis, different HS transformations, … ?
  - Forces?
  - Finite-T generalization [done for *real* HS-fields by Zhang, *PRL* 83, 2777 (1999)]?